Electrosynthesis of lactic acid

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Content

- TNO & VoltaChem
- Background lactic acid
- Technology
- Experiments / results
- Techno-economic evaluation
- Conclusions
SPES TNO
- Carbon capture and storage
- Renewable gas
- Heat storage
- Hydrogen production/use/integration
- Chemicals from biomass
- Electrochemistry

We are working for approx. 3000 companies
Renewable electricity

ECCM report: Berenschot study
• Public-Private *Shared Innovation Program* of ~4 M€ / year, initiated by TNO, ECN and Topsector Chemistry.

• Accelerate innovation and implementation of *electrification & decarbonization* in chemicals.

• Initiate and facilitate *collaborative development* of technology and associated business models.

• Addresses both the *indirect and direct use of electricity* within the chemical industry, involving stakeholders from *chemicals, energy & equipment supply*. 
**Power to chemicals**

- **Electro-organic synthesis**
- **CO$_2$ electro-reduction**
  - Electro-oxidation
  - Electro-reduction

- ✓ Oxidation of furfural
- ✓ Oxidation of hydroxymethylfuran
- ✓ Oxidation of alcohols
- ✓ Reduction of furfural
- ✓ Reduction of hydroxymethylfuran
- ✓ Reductive amination
- ✓ Reduction of oxygen
Focus of TNO: upscaling of electrochemical production processes & TEA
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- Literature study and expert guess
- Downstream processing
- Economical evaluation

Electrochemical systems → Selection and design of electrochemical systems/system development → System integration & demonstration

Lab-scale

Bench-scale

Pilot-scale
Focus of TNO: upscaling of electrochemical production processes & TEA
Lactic acid production: motivation & goals

**GOAL:** demonstration of industrially feasible electrochemical continuous lactic acid production from a renewable feedstock

- LA demand to increase 5-8% yearly, ~400kt/year
- **Renewable feedstock:** biobased glycerol derived 1,2-propanediol (PDO)
- Selective oxidation of alcohol groups is challenge.

New environmentally-friendly circulation

Lactic acid production

- Fermentation (70-90% in 2009)
- Thermocatalytic oxidation on noble metals (Au, Pt, Pd & alloys)
- Electrochemical oxidation on noble metals (Pt, Au) in strong alkaline medium

**Electrochemical production:**
- No use of oxidants & minimal waste
- ~100% conversion
- Stable process
- Ambient conditions
- Control over reaction
- Low product concentration
- Stability of electrodes
- Current densities
**Direct electrolysis of lactic acid**

Screening of direct electrochemical oxidation on

1. **pH<1**
   - Pt, low current densities
   - PbO₂, formic and acetic acids produced

2. **pH>12**
   - Pt, Selectivity 93% LA, 17% acetic acid (2M KOH, 50 °C), low current efficiencies
   - Ni/NiOOH, formic and acetic acids produced

Chadderdon, ACS Catal. 2015, 5, 6926–6936
**Mediated lactic acid electrolysis (TNO patent)**

**Cathode:** $2H^+ + 2e \rightarrow H_2$

**Anode:**
- TEMPO - e $\rightarrow$ TEMPO$^*$
- $C_3H_8O_2 - 4e \rightarrow CH_3CH(OH)COOH$
- $CH_3CH(OH)COOH - 2e \rightarrow CH_3COCOOH$

Oxidation on Carbon based porous electrodes instead of noble metals!
Cyclic voltammetry

Cyclic Voltammetry on graphite, pH 9
- Only borate: no oxidation
- Direct oxidation PDO:
  - Peak potential oxidation PDO: 1.48V
  - Peak potential reduction PDO: 1.26V
- Indirect oxidation PDO (TEMPO added):
  - Peak potential oxidation: 1.31V
  - Peak potential reduction: 1.22V
TEMPO vs ACT

- TEMPO oxidation peak potential 1.34 V vs. RHE
- ACT oxidation peak potential 1.42 V vs. RHE
- Higher current densities with ACT
- ACT cheaper, good replacement
Lactic acid electrolysis

- Anode: carbon felt, ACT
- Anolyte: pH 10 buffer with 0.5 M Na₂SO₄
- RT
- Current density: 5-10 mA/cm²
- Current efficiency: 90% LA
- Yield LA: 80%
Lactic acid electrolysis

- Anode: carbon felt
- Anolyte: pH 10 buffer with 0.5 M Na₂SO₄
- 30 0C
- Current density: 30-40 mA/cm²
- Current efficiency: 70-80%
- Yield LA: 75%
Upscaling ongoing

- Current density >100 mA/cm²
- Yield >90%
- Current efficiency >85%
- Cell voltage <2.5V
- 3D electrodes carbon felt
- Cheap electrolyte Na₂SO₄, no buffer?
- Reactor design: optimization of electrode utilization
- DSP & Electrolyte recycling
Costs

- Total cost 300 Euro/tonne (without DSP)
- Lactic acid price 600-1000 Euro/tonne
- Price of pyruvic acid 5000 Euro/tonne (market?)

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<th>Data used for OPEX calculation*</th>
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<td>Current efficiency</td>
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<td>Reaction yield</td>
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<td>Electricity cost</td>
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<td>Base case cell volt.</td>
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<td>Cell costs</td>
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<td>Factor to other costs</td>
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Paired-electrolysis: proof-of-concept

- Production of lactic acid on both sides of the cell
- Homogenous catalyst required to catalyse peroxide mediated oxidation of PDO to LA
- Cathode: CE H2O2 71%, Yield LA 6%
- Anode: CE 75%, Yield LA 80%
Paired-electrolysis: proof-of-concept

- Production of lactic acid with co-production of CO
- Pt anode replaced with graphite & cell voltage lowered -> halving CO electrolysis costs
- CO current efficiency to be optimized
- Process upscaling strategy

\[
\text{CO}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}
\]
Summary

- Electrochemical lactic acid produced in aqueous electrolytes and ambient conditions with high current efficiencies, 90%, and yields, 80%
- Electrolysis is cost efficient (~300 Euro/tonne), DSP research ongoing
- Paired electrolysis in order to improve business case. Proof-of concept for:
  - Lactic acid production on both electrodes
  - CO co-production on cathode
- Next step, reaction and process optimization and up-scaling
Thank you for your attention!

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